Infrared Absorption Spectra

Some Long-Chain Fatty Acids, Esters, and Alcohols

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Infrared absorption spectra from 2 to 15 microns are given for a number of pure long-chain saturated and monounsaturated fatty acids, methyl esters, triglycerides, and alcohols. The four classes of compounds studied are readily distinguished by spectral features common to the members of each class. Within each class, trans compounds are readily distinguished from cis and/or saturated compounds, but the two last-named types can be differentiated only by careful examination of their spectra. Distinction between individual cis or trans or saturated compounds within a class also requires careful study of the spectra. Terminally unsaturated compounds are readily distinguished from the internally unsaturated and/or the saturated types. Correlations of absorption bands with molecular structure are given for all spectra. The spectra should be useful in the application of the infrared method to studies involving fats and other long-chain systems.

AS A preliminary step in the application of infrared spectroscopy to a variety of problems being conducted in the authors' laboratories, and in particular to studies of the reaction of fatty materials with oxygen, it was necessary to obtain reference spectra from 2 to 15 microns on a wide variety of pure long-chain compounds. With few exceptions (1, 21) published spectra on long-chain aliphatic compounds cover a limited range (10, 18, 20) or the purity of the starting materials is unknown (3).

In this paper, infrared absorption spectra from 2 to 15 microns are reported for some pure long-chain monounsaturated and saturated fatty acids, esters (methyl esters and triglycerides), and alcohols. Interpretations of these spectra have been made on the basis of correlations evident from the absorption curves in conjunction with both published and unpublished infrared data.

EXPERIMENTAL

Spectrophotometer. All spectra were automatically recorded with a Beckman IR-2 infrared spectrophotometer housed in an air-conditioned room and maintained at 25° ± 0.1° C. by the constant temperature circulating bath supplied with the instrument. The slits were automatically adjusted during operation with the aid of a mechanical slit drive (25). Reproducibility of slit widths was equal to that attainable by manual settings. The instrument was calibrated by means of known absorption bands of carbon dioxide and ammonia.

Liquid samples were run directly in a 0.03-mm. standard Beckman liquid cell consisting of two rock salt windows separated by an amalgamated copper spacer; solids were run as dilute solutions in carbon bisulfide in a 1-mm. standard Beckman cell. Exact cell thicknesses, determined interferometrically (27), were 0.0321 and 1.0538 mm. Per cent transmittance curves for the solid samples were obtained by plotting ratios of recorder deflections for solution plus cell to the corresponding deflections for the cell filled with pure carbon disulfide. A similar procedure was employed for the liquid samples, except that a rock salt plate equal in thickness to the combined thicknesses of the two cell windows was used as reference blank.

Materials Used. The reference compounds employed, some of their characteristics, and methods of preparation are shown in Table I.

RESULTS

Figures 1 to 4 show spectra for the various compounds as plots of per cent transmittance against wave length on a uniform wavelength scale. Sample form is indicated on the right side of each figure and wave-length positions of absorption maxima are tabulated on each curve.

Correlation of Absorption Bands with Molecular Structure. Most of the absorption bands appearing in these spectra can be
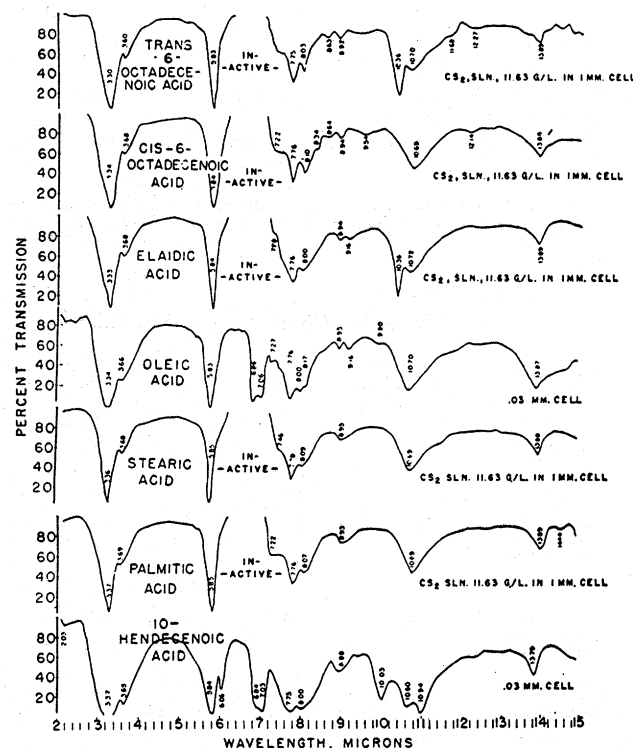

Figure 1. Infrared Absorption Spectra of Pure Long-Chain Monounsaturated and Saturated Fatty Acids

related to specific structural features of the molecules. The assignments made in the following discussion are based on a comparative study of these and a number of the authors' unpublished infrared spectra, together with generalizations drawn from published frequency correlation charts (4, 31) and other data from the literature cited. Although most of these assignments are believed to be reliable, some must be considered tentative, particularly those relating to carbon-oxygen absorption in the 8-micron region and hydroxyl bending vibrations.

Spectral Features Common to All Compounds. The following absorption bands occur at nearly constant wave length in the spectra of all compounds studied, except 10-hendecenoic acid, regardless of class:

1. A strong band near 3.3 microns. In the methyl esters, triglycerides, and alcohols, this band is due entirely to C—H stretching vibrations; in the acids, however, as explained below, absorption due to stretching vibrations of the bonded hydroxyl group (O—H. . . .O) combines with that due to C—H to produce the total absorption observed in this region.
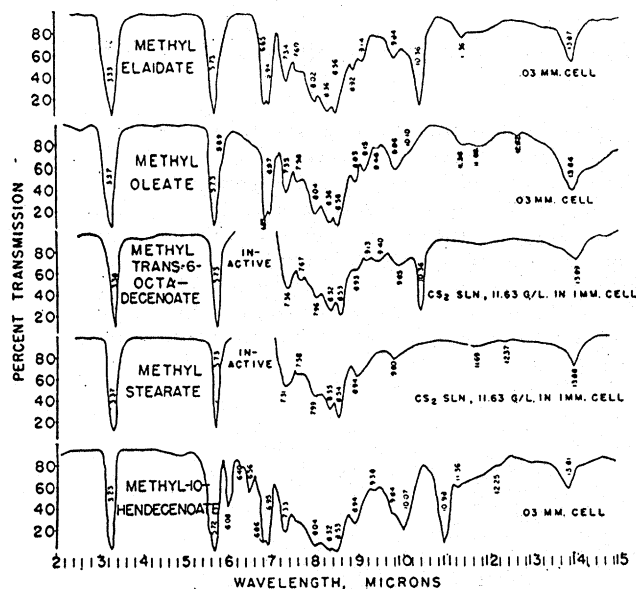

Figure 2. Infrared Absorption Spectra of Pure Long-Chain Monounsaturated and Saturated Methyl Esters

2. A single or doublet absorption near 6.9 or 6.9 and 7 microns related to C—H bending (4, 31). This absorption does not appear in the case of solids, run as dilute solutions in the thick cell, as complete absorption of the solvent rendered the instrument inactive in this region.

3. A band (or inflection) ranging in wave length from about 7.2 to 7.4 microns caused by symmetrical deformation vibrations of the methyl group (32), with the exception of 10-hendecenoic acid, which does not contain this group.

4. A band near 13.9 microns. A band near this wave length has been observed in spectra of a large number of hydrocarbons containing a continuous chain of four or more carbon atoms (32) and recently has been ascribed to a CH_2 wagging mode (23). In the cis monounsaturated compounds, out-of-plane bending vibrations of the hydrogens attached to the double bond carbons probably contribute to the total absorption observed in this region.

Spectral Features Common to Members of Each Class. In addition to the common bands discussed above, the individuals within each of the four classes of compounds studied show a number of common spectral features which serve for class distinction.

LONG-CHAIN FATTY ACIDS (Figure 1). The band near 3.7 microns occurring on the long wave-length side of the strong C—H stretching absorption has been observed in the spectra of a number of organic acids and has been attributed to the presence of the carboxyl group in such compounds (2). The presence of this band, as well as the absence of any resolved O—H stretching band near 3 microns, is explained by the fact that carboxylic acids associate through the formation of hydrogen bonds, even at fairly high dilution in nonpolar solvents (12, 13). In the lower fatty acids and at least one higher acid (lauric) (10, 18, 20), infrared absorption measurements in the 3-micron region have been employed by a number of investigators (9, 11–15) in the study of this association. In general, these and similar studies show that, although the normal free O—H stretching band in the monomeric acid molecule occurs near 2.8 microns, in the dimer (associated) molecule the absorption maximum due to O—H...O "fuses" into the C—H absorption near 3.3 microns and extends to somewhat longer wave length. Thus, we conclude that the 3.7-micron band in the long-chain fatty acid spectra represents a branch of the O—H...O "association" band and that the main branch of this band combines with the C—H stretching band to produce the total absorption seen near 3.3 microns.

In addition to the 3.7-micron band, the authors have observed that the strong broad absorption seen near 10.7 microns occurs in the spectra of a variety of carboxylic acids. Davies and Sutherland (11) have suggested that a band near this wave length in the lower fatty acids may arise from vibrations of the O—H group in and out of the plane of the carboxyl group. Both bands disappear on esterification of the acids (Figure 2).

The doublet absorption about 7.8 and 8.0 microns is another general characteristic

Table I. Characteristics of Reference Compounds

Reference Compound	B. P.		M. P., ° C.	n_D^{30}	Iodine No.	Neut. Equiv.	Sapon. Equiv.	Method of Preparation and/or Literature Reference
	° C.	Mm.						
Oleic acid	208	4	...	1.4564	90.0–90.3	...	...	(8, 30)
Elaidic acid	...	...	44	...	89.5	...	...	(6, 7)
Palmitic acid	...	...	62.1–62.5	...	...	256.3	...	(28)
Stearic acid	...	...	69.4–69.6	...	...	282.4	...	(28)
Petroselinic acid (cis-6-octadecenoic acid)	...	...	30.5–31.0	...	88.8	...	...	From celery seed oil by methanolysis, fractional distillation, and recrystallization of C-18 acids from acetone
Petroselaidic acid (trans-6-octadecenoic acid)	...	...	52.8–53.2	...	89.8	...	...	From petroselinic acid by isomerization with selenium (6, 7)
10-Hendecenoic acid	180	26.5	24.3–24.5	...	138	185	...	(16)
Methyl oleate	180	4	...	1.4484	...	...	...	Esterification of pure acid
Methyl elaidate	180	4	...	1.4492	...	...	...	Esterification of pure acid
Methyl stearate	180	4	38.9	...	...	...	...	Esterification of pure acid
Methyl petroselaidate	...	...	...	...	85.0	...	...	Esterification of pure acid
Methyl 10-hendecenoate	142	26	...	1.4349	...	...	...	Esterification of pure acid (16)
Trielaidin	...	...	41.3–41.5	...	...	...	...	Reaction of acid chloride (5) with glycerol in pyridine solution
Trimyristin	...	...	58	...	...	...	...	Reaction of acid chloride (5) with glycerol in pyridine solution
Triolein	...	...	...	...	85.1	...	...	Reaction of acid chloride (5) with glycerol in pyridine solution
Mixed palmitostearins	...	...	62.7–62.9	...	...	...	291	Recrystallization of completely hydrogenated vegetable oil from acetone
Oleyl alcohol	180	3.7	...	1.4562	93.7	...	...	(30)
Elaidyl alcohol	...	...	35.7–35.9	...	93.7	...	...	(29)
n-Octadecyl alcohol	...	...	58	...	...	...	...	Recrystallization of purest commercial grade

of long-chain fatty acids. Absorption in this region is common to a large number of compounds containing a C—O linkage in which the carbon atom is unsaturated (*4*, *31*). Although a survey of the literature indicates disagreement in the assignment of C—O frequencies in lower fatty acids (*11*, *14*), it seems probable that one or both of these bands in the long-chain acids must be related to vibrations involving the C—O linkage in

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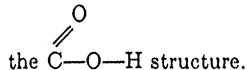
the C—O—H structure.

The strong band near 5.8 microns is, of course, due to C=O stretching vibrations. The exact position of this band (5.83 to 5.85 microns) in the long-chain acids is characteristic and distinct from that in the methyl esters and triglycerides (5.71 to 5.75 microns).

METHYL ESTERS OF LONG-CHAIN FATTY ACIDS (Figure 2). Esterification of the long-chain fatty acids produces marked changes in the absorption characteristics. As noted above, the 10.7- and 3.7-micron bands disappear; the C=O stretching band which appears at 5.83 to 5.85 microns in the acids is shifted to 5.72 to 5.75 in the ester spectra. This shift of about 0.1 micron is general in the esterification of long-chain acids.
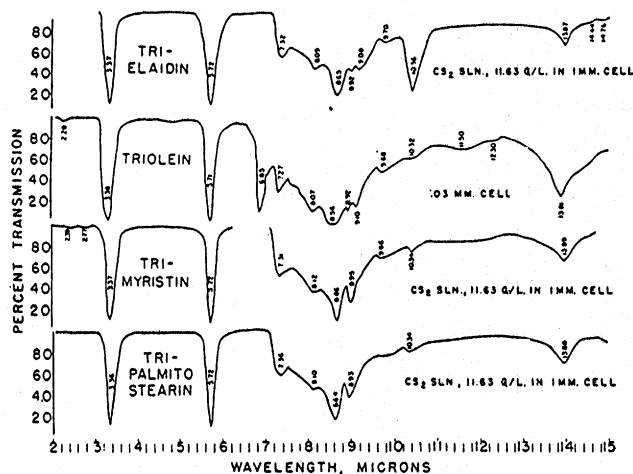

Figure 3. Infrared Absorption Spectra of Pure Long-Chain Triglycerides

The strong triplet absorption at about 8.0, 8.3, and 8.5 microns is a characteristic feature of the spectra of methyl esters of long-chain acids. One or more of these bands must be related in this case to vibrations involving the C—O linkage in the ester group

$$\overset{O}{\underset{\displaystyle /\!\!/}{}} C\!-\!O\!-\!CH_3;$$

the replacement of $\overset{O}{\underset{\displaystyle /\!\!/}{}}C\!-\!OH$ with $\overset{O}{\underset{\displaystyle /\!\!/}{}}C\!-\!O\!-\!CH_3$ has resulted in considerable alteration in the position and general pattern of the absorption involving C—O links.

TRIGLYCERIDES OF LONG-CHAIN FATTY ACIDS (Figure 3). The triglycerides are readily distinguished from the acids or methyl esters by their characteristic absorption. The position of the C=O stretching band corresponds closely to that observed in the methyl esters, but the nature of the absorption in the 8-micron region, some or all of which must be attributed in this case to the presence of C—O linkages in the triester structure, is considerably altered. This general absorption pattern, comprising a strong band near 8.6 microns flanked by weaker bands near 8 and 9 microns, is common to all triglycerides of long-chain fatty acids whose spectra the authors have examined.

LONG-CHAIN ALCOHOLS (Figure 4). Because a large number of hydroxy compounds show strong absorption in the 9- to 10-micron region of the infrared (*4*, *31*), the strong band near 9.5 microns in the spectra of Figure 4 may be attributed to the alcoholic hy-

droxyl group in these compounds. This band may possibly arise from bending motions of the OH group in the CH_2—OH structure.

The O—H stretching absorption in the two solid alcohols, elaidyl and stearyl (run in dilute solution), appears as a weak band near 2.7 microns, indicating a normal "free" alcoholic O—H vibration (*10*). In the spectrum of oleyl alcohol (run as the pure liquid), this absorption occurs at about 3 microns and is much more intense relative to the adjacent C—H absorption, indicating strong hydrogen bonding in the condensed phase, as expected (*10*). On dilution, the "association" band decreases in intensity (relative to C—H) and shifts to the normal 2.7-micron position.
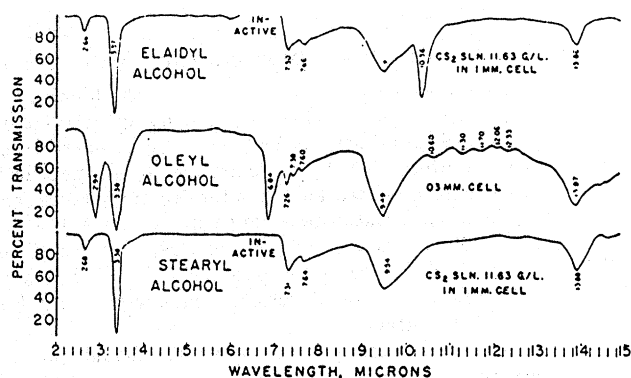

Figure 4. Infrared Absorption Spectra of Pure Long-Chain Alcohols

Spectral Differences within Each Class. In addition to the common features which distinguish each of the four classes of long-chain compounds, significant spectral differences are apparent within each class. These may be summed up and interpreted as follows:

DIFFERENCES RELATED TO C—H BENDING VIBRATIONS AT DOUBLE BOND. All the trans monounsaturated compounds, regardless of class, show a strong absorption band at 10.36 microns, but this band is absent in the cis monounsaturated and saturated compounds (Figures 1 to 4). Recent studies (*17*, *22*) indicate that this band is common to a variety of monounsaturated hydrocarbons and other compounds having the trans configuration at the double bond. The band undoubtedly arises from out-of-plane vibrations of the two hydrogen atoms attached to the double bond in a trans structure (*24*). The corresponding hydrogen-bending vibrations in a cis monounsaturated compound do not seem to give rise to appreciable absorption in this region. This absorption in hydrocarbon spectra has recently been found to occur in the 14- to 16-micron region (*17*, *22*). In the present case, comparison of the spectra of the Δ^9 cis-trans methyl ester pair and the Δ^6 cis-trans acid pair shows the absorption in the 13.8- to 14.3-micron region to be greater for the cis compound in each case. The Δ^9 cis-trans acid, glyceride, and alcohol pairs cannot be directly compared in this respect. The ratio of the absorption intensity in this region to that at the C=O stretching peak, however, is greater for the cis acid and glyceride than for the trans acid and glyceride. Thus it would seem that the absorption near 13.9 microns in cis compounds is due only partly to a methylene group "wagging" mode (see above); the remainder is contributed by the bending vibrations of the two hydrogens attached to the double bond carbons.

In the acid and methyl ester series (Figures 1 and 2), the terminally unsaturated compounds (10-hendecenoic acid and its methyl ester) show two strong bands near 10 and 11 microns, which are absent in the internally unsaturated acids and esters. The assignment of bands near these wave lengths to bending motions of the hydrogens attached to a terminal double bond is well known (*24*) and seems firmly established.

DIFFERENCES RELATED TO C=C STRETCHING VIBRATIONS. The two terminally unsaturated compounds mentioned above (Figures 1 and 2) show a well resolved C=C stretching band near 6 microns, but no resolved band appears at this wave length in the spectra of the various internally unsaturated compounds shown in Figures 1 to 4. Close examination of the spectra of the cis monounsaturated compounds of Figures 1 to 4 reveals that a slight broadening or inflection on the long wave-length side of the strong C=O band is the only evidence of C=C stretching absorption under the resolution employed. The prediction from theoretical considerations, that C=C stretching should be infrared active near 6 microns in a cis but not in a trans compound, was confirmed in the case of the ethyl esters of oleic and elaidic acids by McCutcheon, Crawford, and Welsh (20), but to bring out this difference they found it necessary to plot the ratio of the transmittance of each of the esters to that of ethyl stearate in the 6-micron region.

GENERAL COMMENTS AND CONCLUSIONS

The foregoing discussion shows that the four classes of long-chain compounds studied are readily differentiated by their characteristic infrared absorption. Within each class, the trans monounsaturated compounds are readily distinguished from the cis monounsaturated and/or saturated compounds, and internal and external unsaturation can easily be differentiated. Because of the close similarity of their spectra, however, distinction between cis and saturated, or between various individual cis, trans, or saturated compounds within a class requires careful examination of the curves.

In general, the spectra presented should prove useful in assessing the potentialities of the infrared method as applied to studies of fat systems; they are primarily intended to serve as a guide in the development of spectroscopic or combined chemical-spectroscopic methods for the analysis of mixtures of fatty materials. For example, as a result of this study, the authors have developed an infrared spectrophotometric method for determination of trans components in mixtures of long-chain compounds, utilizing the strong 10.36-micron band (26).

Although the structural correlations given are not all firmly established, when applied with caution they should be useful in the detection and possibly the estimation of functional groups in fats and other long-chain systems.

ACKNOWLEDGMENT

LITERATURE CITED

(1) Am. Petroleum Inst., A.P.I. Project 44, Spectra, National Bureau of Standards.
(2) Anderson, J. A., and Seyfried, W. D., ANAL. CHEM., 20, 998 (1948).
(3) Barnes, R. B., Gore, R. C., Liddel, U., and Williams, V. Z., "Infrared Spectroscopy," New York, Reinhold Publishing Corp., 1944.
(4) Barnes, R. B., Gore, R. C., Stafford, R. W., and Williams, V. Z., ANAL. CHEM., 20, 402 (1948).
(5) Bauer, S. T., Oil & Soap, 23, 1 (1946).
(6) Bertram, S. H., Chem. Weekblad, 33, 3 (1936).
(7) Bertram, S. H., Oil Colour Trades J., 94, 1227 (Oct. 8, 1938).
(8) Brown, J. B., and Shinowara, G., J. Am. Chem. Soc., 59, 6 (1937).
(9) Buswell, A. M., Rodebush, W. H., and Roy, M. F., Ibid., 60, 2239 (1938).
(10) Davies, M. M., J. Chem. Phys., 8, 577 (1940).
(11) Davies, M. M., and Sutherland, G. B., Ibid., 6, 755 (1938).
(12) Gillette, R. H., J. Am. Chem. Soc., 58, 1143 (1936).
(13) Gillette, R. H., and Daniels, F., Ibid., 58, 1139 (1936).
(14) Herman, R. C., and Hofstadter, R., J. Chem. Phys., 6, 534 (1938).
(15) Ibid., 7, 460 (1939).
(16) Jordan, E. F., and Swern, D., J. Am. Chem. Soc., 71, 2377 (1949).
(17) Kitson, R. E., Experimental Station, E. I. du Pont de Nemours & Co., Wilmington, Del., private communications.
(18) Klotz, I. M., and Gruen, D. M., J. Phys. & Colloid Chem., 52, 961 (1948).
(19) Knight, H. B., and Swern, D., J. Am. Oil Chemists' Soc., 26, 366 (1949).
(20) McCutcheon, J. W., Crawford, M. F., and Welsh, H. L., Oil & Soap, 18, 9 (1941).
(21) Rao, P. C., and Daubert, B. F., J. Am. Chem. Soc., 70, 1102 (1948).
(22) Rasmussen, R. S., Brattain, R. R., and Zucco, P. S., J. Chem. Phys., 15, 135 (1947).
(23) Sheppard, N., and Sutherland, G. B., Nature, 159, 739 (1947).
(24) Sheppard, N., and Sutherland, G. B., Proc. Roy. Soc., A196, 195 (1949).
(25) Shreve, O. D., and Heether, M. R., ANAL. CHEM., 22, 836 (1950).
(26) Shreve, O. D., Heether, M. R., Knight, H. B., and Swern, D., Ibid., in press.
(27) Smith, D. C., and Miller, E. C., J. Optical Soc. Am., 34, 130 (1944).
(28) Swern, D., and Jordan, E. F., J. Am. Chem. Soc., 70, 2334 (1948).
(29) Swern, D., Jordan, E. F., and Knight, H. B., Ibid., 68, 1673 (1946).
(30) Swern, D., Knight, H. B., and Findley, T. W., Oil & Soap, 21, 133 (1944).
(31) Thompson, H. W., J. Chem. Soc., 1948, 328.
(32) Thompson, H. W., and Torkington, P., Trans. Faraday Soc., 41, 246 (1945).